metal 15Kh19N9M4S5G3D. This material is not inferior in heat resistance at dramatic thermal cycles and in score resistance to known chrome-nickel alloys containing boron and silicon, and is much superior to metal 13Kh16N8M5S5G4B (hard-facing with electrodes TsN-12M and their analogues). As to a number of service properties and price, chromium steel 22Kh16N2M is fully acceptable for hard-facing of sealing surfaces of components of general-engineering fittings, which are used at a temperature of up to 400 °C and pressure of 16 MPa.

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PARTICLE DISPERSITY AND MANGANESE VALENCE IN WELDING AEROSOL

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Method of X-ray photoelectron spectroscopy was used to establish the valent state of manganese compounds in the welding aerosol. Valent state of manganese compounds (Mn^{+4}) was found in welding with basic electrodes. Analysis of dispersity of welding aerosol solid compound was performed using the method of laser granulometry.

Keywords: *arc welding, coated electrodes, solid component of welding aerosol, particle dispersity, bimodal distribution, agglomerates, manganese valence*

In welding of carbon low-alloyed steels, manganese compounds are the most hazardous components of the solid component of welding aerosol (SCWA) [1, 2]. Toxicity of these compounds, in its turn, depends on manganese valence and increases with the increase of its oxidation level. Threshold limit values (TLV) of manganese and its compounds in the welding aerosol (WA) in the working zone air are equal to 0.6/0.2 and 0.3/0.1 mg/m^3 (numerator shows the maximum one time, and the denominator — shift average TLV) at its content in WA below 20 % and from 20 up to 30 %, respectively [3]. Modern norms of manganese TLV in WA and recommendations do not separate manganese compounds by valence and establish one TLV norm equal to 0.2 mg/m^3 [4, 5]. Manganese in WA belongs to the second hazard class [3].

A number of investigations devoted to study of SCWA composition [1, 6–9] showed that the most probable manganese state is Mn^{2+}, Mn^{3+}.

Staff members of the E.O. Paton Electric Welding Institute and I.M. Frantsevich Institute of Problems of Materials Science studied the valent state of manganese in aerosols formed in welding with electrodes with coating of rutile and basic types. Investigations were performed using X-ray photoelectronic spectrometer ES-2401.

Investigations were performed using SCWA forming in welding with test electrodes with coating of rutile (electrode index E4) and basic types (electrode index PSh4 and PSh5). Here, SCWA for analysis were selected by deposition on a filter, mechanical removal from the filter and placing into a brass weighing bottle with subsequent filling of the latter by argon to prevent final oxidation of samples at contact with ambient oxygen. Spectra were excited by non-monochromatized radiation of MgK_α-lines. SCWA were rubbed into the copper plate surface, which was first ground and etched by nitric acid. Studied samples completely covered the copper plate, so that lines corresponding to copper atoms were not observed in the plain spectra. Mn2*p*- and Mn2*p*-spectra were filmed in the plain mode and optimum mode of Mn2*p*-spectra measurement was selected for investigations. By the results of obtained Mn3*p*-spectra (Figure 1, *a*) it was established that manganese in SCWA of electrodes with basic type coating (PSh4, PSh5) is present in valent state +4 (peak *I*), and in SCWA of electrodes with a

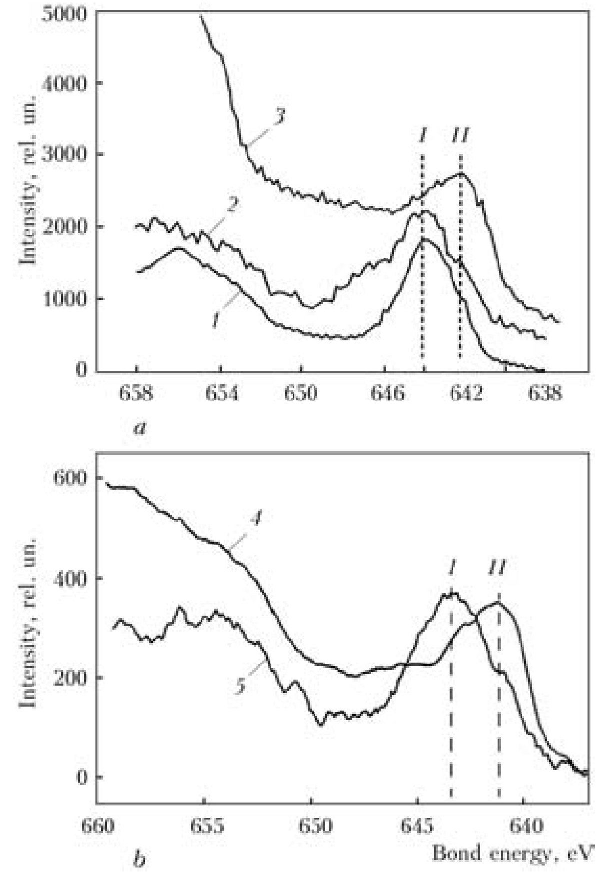

Figure 1. Comparison of XPES spectra of SCWA of electrodes with coatings of basic PSh4 (*1*), PSh5 (*2*) and rutile E4 (*3*) types (*a*) and commercial electrode grades MR-3 (*4*) and UONI-13/55 (*5*) (*b*) (for *I*, *II* designations see the text)

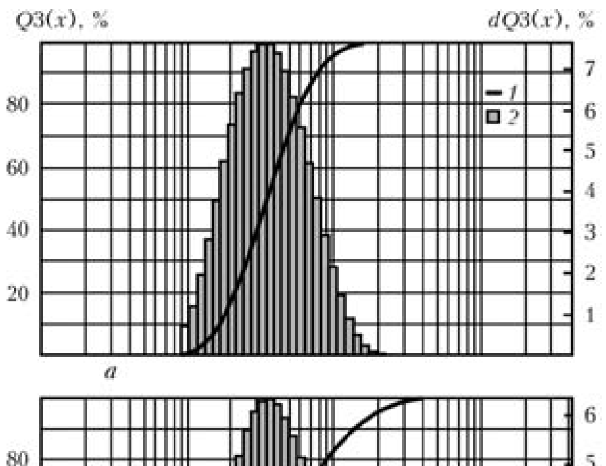

Figure 2. Volume distribution $Q3(x)$ (*1*) and distribution density $dQ3(x)$ (*2*) of dispersity of SCWA of electrodes with coating of basic UONI-13/55 (*a*) and rutile MR-3 (*b*) types

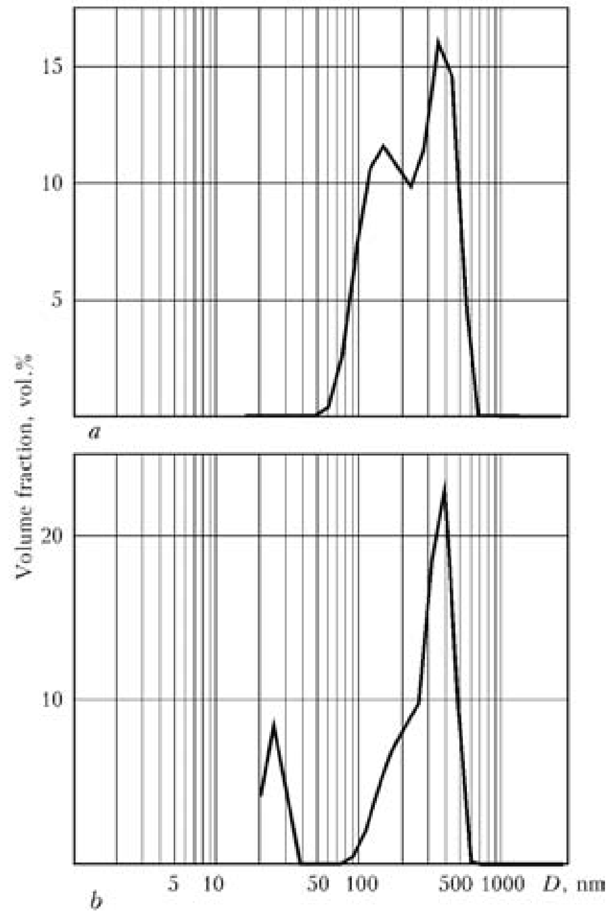

Figure 3. Volume distribution of SCWA dispersity of electrodes with coating of rutile MR-3 (*a*) and basic UONI-13/55 (*b*) type

rutile-type coatings (E4) it is present in valent state +3 (peak *II*).

Experimental data obtained on test electrodes were confirmed at X-ray photoelectronic spectrometric (XPES) investigations of valent state of manganese in SCWA of commercial grade electrodes UONI-13/55 and MR-3 (Figure 1, *b*). The given data are indicative of the presence of four-valent manganese in SCWA formed in welding with basic electrodes.

An important factor determining SCWA toxicity is dispersity of WA particles. Particles of less than 20 μm diameter can remain suspended in the air. 100 % of particles of less than 1 μm diameter penetrate into the body through the respiratory tract [10]. About 30 % of particles of 0.1–1.0 μm size precipitate in the lungs. Particles of less than 0.1 μm size (100 nm) are also inhaled and precipitate in the lungs. Penetration of nano-sized particles through the skin [11], as well as their penetration into the brain through the nerves in the nasal sinuses is possible [12, 13].

Most of the recent research was conducted using cascade impactors, operating by the method of aerodynamic separation [7, 9, 14–16].

In this work SCWA dispersity was assessed by the method of laser granulometry with Analysette 22 MicroTec Plus analyzer of «Fritsch» Company (measurement range of 0.08–42 μm). Studied were SCWA generated in welding with basic and rutile electrodes. WA extracted from the filter, were stored in a glass weighting bottle. In preparation for analysis the sample was mixed with a spatula, which was followed by placing it into a beaker, where distilled water with SAS (0.1 % solution of sodium pyrophosphate) was added. The suspension was mixed for three minutes in an ultrasonic dispenser Ultrasonic Bath LABORETTE 17. Before suspension analysis it was checked for stability.

Each sample was analyzed three times. Figure 2 gives the results of measurements and calculations. Volume distribution of particles was calculated using Fraunhofer theory. Results of investigation of SCWA dispersity were as follows. In UONI-13/55 electrodes the volume of particles of less that 10 μm diameter is equal to 0.2 %; those of less than 50 μm diameter — 0.4 %, and those of less than 90 μm diameter — 0.8 %. In MR-3 electrodes particles smaller than 10 μm amount to 0.2 %, those smaller than 50 μm — 0.4 %; those smaller than 90 μm — 1.4 % in the first two measurements, and 1.3 % in the third measurement, respectively. From the above data it is seen that the average diameter of aerosol particles in electrodes of both basic and rutile type is in the range of 0.3–0.4 μm (peak of histograms of distribution density $dQ3(x)$ in Figure 2). SCWA of MR-3 electrodes also have a higher percentage of coarser particles.

Presented results give a general idea of SCWA dispersity. For a more detailed analysis of the nanorange of particles, which present a particular hazard because of a higher ability of penetration into the welder's body, analysis was performed in Zetasizer 1000HS instrument (measurement range of 0.002–3 μm) at the I.M. Frantsevich Institute of Problems of Materials Science.

Studied were SCWA generated in welding with electrodes with coating of basic (UONI-13/55) and rutile (MR-3) types. WA extracted from the filter were mechanically crushed and poured into a plastic container filled with distilled water with SAS (1 % solution of sodium hexametaphosphate). The suspension was stirred for 10 min in ultrasonic dispenser UZDN-A. Several drops of the obtained suspension were added to the cuvette filled with dispersion medium for 2/3. The cuvette was placed into the instrument, where the degree of saturation of the analyzed solution was determined during initial analysis.

During analysis of each sample PC was used to perform three calculations, each of which was conducted proceeding from the results of ten measurements with determination of an average value. Results of measurements and calculations are given in Figure 3 and in the Table. Average time of analysis of one sample was equal to 25 min. Volume distribution of particles was calculated using Mie theory.

Obtained data indicate that SCWA of both electrode types have a bimodal particle distribution by dimensions. Average diameter of WA particles for MR-3 and UONI-13/55 electrodes is equal to 209.8 and 236.1 nm.

Particles of WA of MR-3 electrodes form agglomerates with average size of 150±60 and 370±120 nm, and primary particles are not clearly defined. Primary WA particles of UONI-13/55 electrodes have a narrow distribution, their average size is about 25±6 nm.

Results of analysis of SCWA dispersity

Peak	Area, arb. un.	Average, nm	Width, nm
Peak analyses by intensity			
I	100.0/99.9	236.2/259.9	243.4/220.6
Peak analyses by volume			
I	48.0/16.8	156.5/25.6	96.5/6.0
II	52.0/83.2	370.1/318.2	243.1/212.1
Peak analyses by quantity			
I	100.0/99.4	129.8/25.6	85.0/6.0

Note. Numerator gives data for MR-3 electrodes, denominator — for UONI-13/55.

A susceptibility to formation of agglomerates of 320±100 nm size was observed.

CONCLUSIONS

1. Mn^{+4} compounds were found in aerosols formed in welding with basic electrodes.

2. SCWA, formed in welding with electrodes with coatings of basic and rutile types, have a bimodal distribution by dimensions.

3. WA particles of both types form agglomerates at cooling.

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